

Tin dioxide thin film gas sensor prepared by CVD : Influence of grain size and thickness on the electrical properties

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Introduction

In order to have a better understanding of phenomena which can occur in tin dioxide gas sensors, the influence of structural parameters on the electrical response has been investigated. It was first Ogawa who studied the conductivity variations of tin dioxide ultrafine particle films deposited by reactive evaporation [1]. He presented a conduction model in which the relative size of the particles D and the Debye length L (depletion layer) explain the increase of sensitivity when the grain size D is comparable to L .

Recent works about the role of grain size on the electrical conductance and gas sensitivity have been carried out by Yamazoe [2], and a comprehensive model based on a grains geometry linked together by necks proposed.

Concerning the influence of thickness on the conductance, several studies have been made on films deposited by various methods, but no general trend has emerged and no satisfactory model has been proposed.

Our previous studies on tin dioxide sintered powder have pointed out the effect of grain size and grain boundaries on the electrical conductivity [3], and we have now concentrated our efforts on tin dioxide thin films elaborated by reactive evaporation [4], and more recently by CVD. The influence of deposition parameters (total pressure, oxygen pressure) in the reactive evaporation process has been correlated with the film density and the electrical performances.

One of the most interesting advantages in the choice of the CVD method, if we compare with physical methods such as sputtering, is the possibility to change the morphology and the structural properties of the films by varying the deposition parameters. This is particularly the case with the deposition temperature, which brings the activation energy of the chemical reaction, as it has been demonstrated by several techniques (XRD, TEM, ESCA, ...).

The aim of this paper is to correlate the structural properties of the CVD-deposited SnO_2 films (essentially grain size and thickness) to electrical properties such as conductance and gas sensitivity.

Experiments

Film preparation

Tin dioxide thin films are elaborated by an OMCVD method previously described [5]. The organometallic precursor, dibutyl tin diacetate (DBTD), is transported in vapor phase by a nitrogen flow, mixed with oxygen in excess, and introduced under low total pressure (1 mbar) into the reactor. The tin compound oxydation takes place at the surface of a furnace in the 300-600°C range. Typical deposition parameters are listed below :

Deposition temperature	350-550°C
Total pressure	0,5-5 mbar
O ₂ flow	50 sccm
N ₂ + DBTD flow	250 sccm
Deposition rate	5-40 Å/mn
Duration	5 mn-1h

Tin dioxide is deposited onto different substrates, depending on the characterization method used : silicon for XRD, SEM and ESCA, glass for thickness measurements, copper or gold carbon-coated grids for TEM, and alumina for electrical measurements.

After deposition, films are annealed in ambient air in order to stabilize the material and to avoid conductance drifts (15 hours at 600°C).

Film characterization

A lot of characterization methods have been used to have the best knowledge of the CVD-deposited material.

Scanning electron microscopy gives macroscopic informations about the film structure. CVD films are very compact, with a granular surface. The growth is columnar, and the adherence to the substrate is very good.

X-ray diffraction analyses show that films deposited at temperature higher than 375°C are crystallized with the cassiterite SnO₂ structure (figure 1). This is confirmed by transmission electron microscopy (TEM) diffraction patterns (figure 2). Films deposited at 325°C are amorphous (diffusion rings), and the crystallization increases with deposition temperature (diffraction spots, representative of the crystal symmetry)

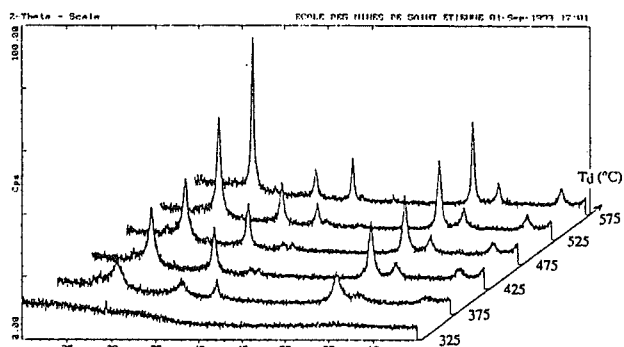
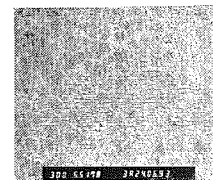
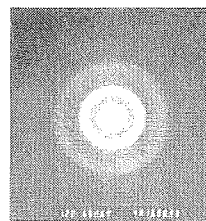


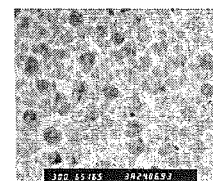
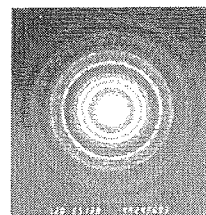
Fig. 1 : Influence of the deposition temperature on the XRD pattern of tin dioxide CVD films

Grain size is measured from X-ray diffraction peaks using the Scherrer formula, in good agreement with sizes estimated from TEM micrographs. These experiments are realized with ultrathin films (100 to 200 Å) directly deposited onto carbon-coated copper grids. Thickness measurements are carried out by X-ray reflectometry at glancing incidence using the Kiessig method [6]. This is an accurate method in the 50-600 Å range.

(1)



(2)



(3)

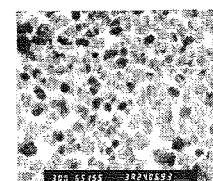
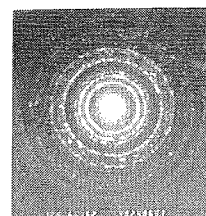


Fig. 2 : TEM diffraction patterns and micrographs of SnO₂ CVD films deposited at : 350°C (1), 450°C (2), 550°C (3)

Auger and ESCA analyses indicate that there is no impurity in the SnO₂ films, excepted some carbon traces located just at the surface. Stoichiometry measurements have been carried out from ESCA spectra by comparing the areas of the O_{1s} and Sn_{3d5/2} peaks. This ratio is corrected by the cross section of the O_{1s} and Sn_{3d5/2} electrons.

Electrical measurements are made by means of a conductivity testing bench [5]. Tin dioxide is deposited onto an alumina substrate (8x8 mm) covered with two gold thin film electrodes. We have verified that this particular geometry with gold electrodes under the SnO₂ film is not responsible for conductance changes with the film thickness, because no difference has been observed with "sandwich" electrodes. Samples are set in a measuring cell where temperature and gaseous atmosphere (humidity and gas concentration) are controlled. Conductance measurements are made using the two probe d.c. method. The sensitivity S is defined as the ratio $(G - G_0)/G_0$ where G and G_0 are the electrical conductance measured under a gas and pure synthetic air respectively.

Results

Influence of grain size

Depending on the conditions of preparation, it is possible by CVD to change the mean grain size in tin dioxide films. The grain size increases with the deposition temperature from 50 to 250 Å when T_d varies between 375°C and 575°C (Figure 3). Films deposited at low temperature ($T_d < 375^\circ\text{C}$) are amorphous. The effect of successive annealings in ambient air on the same films (17 hours at 600°C, then 13 hours at 800°C) corresponds to a slight increase in the grain size.

If we study the influence of deposition temperature on the electrical conductance G_0 measured in synthetic air at 500°C, large variations are observed (several orders of magnitude) and a maximum of conductance appears around 400-450°C (Figure 4).

The conductance versus grain size curve is reported in figure 5.

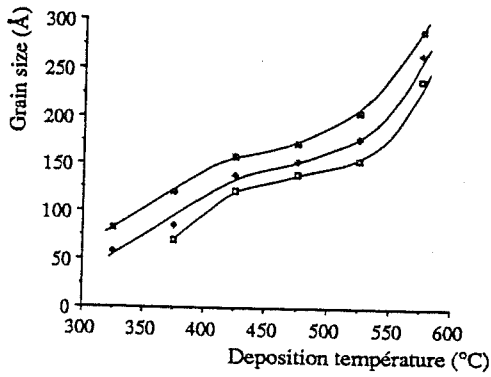


Fig. 3 : Influence of deposition temperature and annealing on the grain size measured by XRD
(1) : no annealing; (2) : 17 h at 600°C;
(3) : 17 h at 600°C + 13 h at 800°C

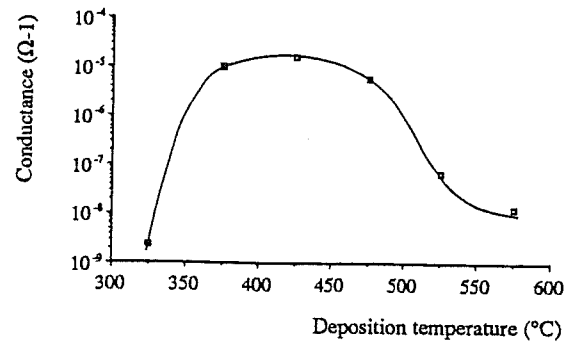


Fig. 4 : Influence of deposition temperature on the electrical conductance G_0 measured under pure air at 500°C

Influence of thickness

The film thickness has a great influence on the electrical properties in tin dioxide CVD films. Indeed, the electrical conductance G_0 measured under synthetic air at 500°C increases over a large scale with the thickness (figure 6). We have verified that the conductivity σ ($\sigma = G/e$), which present the same variations in this thickness range, reach a constant value for thicknesses greater than 3000 Å.

Concerning the gas sensitivity, a maximum is usually observed in the 200-600 Å range with different gases : CH₄ 1000 ppm, CO 300 ppm, or ethanol 100 ppm (Figure 7).

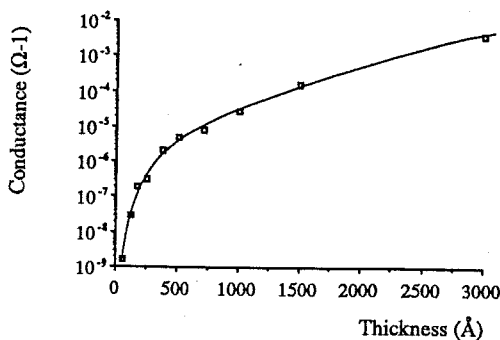


Fig. 6 : influence of film thickness on the conductance G_0

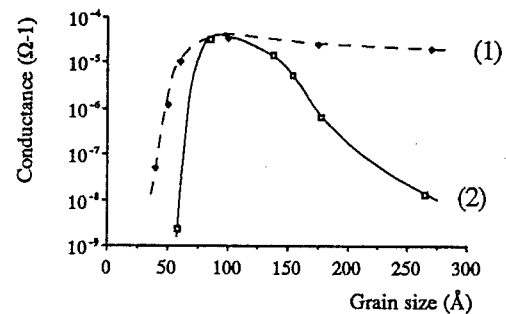


Fig. 5 : Influence of the grain size on the conductance G_0
(1) : from Yamazoe, ref. 2, (2) : our results

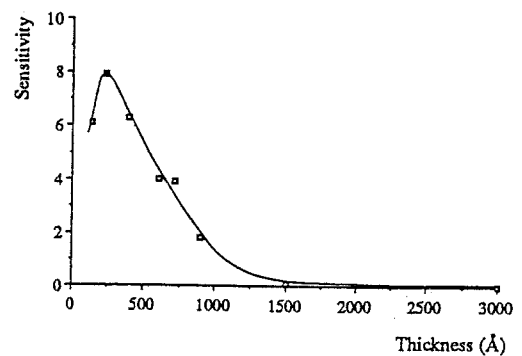


Fig. 7 : Influence of film thickness on the sensitivity S under CH₄ 1000 ppm

Discussion

In the low grain size range, a sharp increase of G_0 occurs from a critical value $D = 70$ Å. Similar variation has already been observed by Yamazoe [2] and explained with a model involving the grain size D and the depletion layer L .

Indeed, SnO₂ is a n-type semiconductor, and the adsorption of oxygen at its surface induces the formation of an electron-depleted space charge layer. The thickness L of this layer has been calculated by Ogawa [1] and is equal to 30 Å for ultrafine particle films obtained by reactive evaporation.

An attentive study of TEM micrographs suggest that grains are linked together by necks, forming agglomerates of several particles (2 to 5 grains). When the grain size D is thinner than twice L , i.e. 60 Å, tin dioxide grains are fully depleted and the material remains highly resistive. When D becomes greater

than $2L$, a conduction channel appears between two adjacent grains in an agglomerate, corresponding to an important increase of conductance. In this grain size range, the grain boundaries resistances are supposed to be negligible with respect to the resistance changes which occur into intrinsic grains.

This model is well adapted in our case to explain the conductance variations for small grains (50 to 100 Å), but it is not sufficient for grain sizes greater than 100 Å. Indeed, in Yamazoe's model, when the crystallite size D is greater than $2L$, the conductance is controlled by grain boundaries and remains at a constant value (see figure 5).

In our case, the grain size increase, which is due to the deposition temperature, is not the only structural parameter varying. The texture of the material changes from a continuous and amorphous structure at low temperature to a well-crystallized structure with distinct grains at high temperature, as it can be seen on TEM micrographs (Figure 2).

Moreover, stoichiometry measurements of SnO_x films from ESCA spectra show that the x coefficient increases with the deposition temperature (Figure 8).

It is well known that the conductivity σ in tin dioxide is mainly due to oxygen vacancies. When the stoichiometric coefficient x is close to the ideal value $x = 2$, the concentration of oxygen vacancies decreases. We can therefore think that the stoichiometry variations are responsible for the conductance decrease. The same evolution is also observed during the annealing phase : stoichiometry measurements show that the x increase, i.e. the decrease of oxygen vacancies, is correlated with a decrease of conductance (figure 9).

In an other way, Hall effect measurements on tin dioxide CVD films have been carried out by Kojima [7], and similar variations of the conductivity versus deposition temperature have been observed, with a maximum around 450°C. These variations are explained with the grain boundary model, and considering also homothetic variations of the carrier concentration n_c with the deposition temperature.

The stoichiometry variations, corresponding to the carrier concentration variations measured by Kojima, could be responsible of the difference in behaviour of the $G=f(D)$ curves observed by Yamazoe and our results (Figure 5).

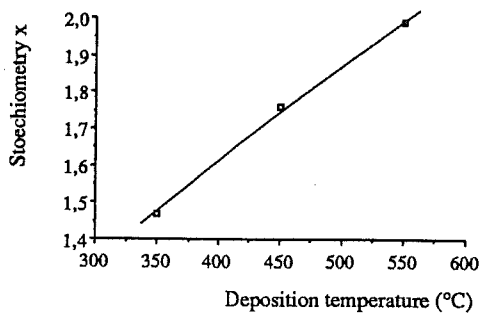


Fig. 8 : Influence of deposition temperature on the stoichiometry of CVD films from ESCA measurements

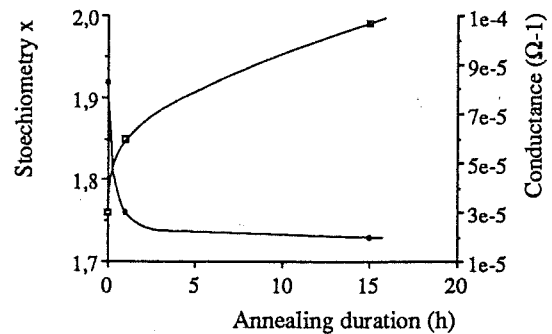


Fig. 9 : Influence of annealing duration at 600°C on the stoichiometry x and the electrical conductance G_0

Concerning the influence of thickness on the electrical conductance, the regular increase of G_0 with e has always been observed whatever the deposition parameters are, i.e. for films having different morphologies and structural properties (stoichiometry, grain size). The conductance increase for CVD films up to a sufficient thickness (around 3000 Å), is probably due to an increase of the number of percolation paths between tin dioxide grains.

Indeed, CVD SnO_2 films are formed by the piling up of grains linked by necks or grain boundaries, and the electrical conduction takes place through preferential percolation paths where the resistivity is the lowest. In the thinnest films, the material is not well organized, and there are only few percolation paths. When the thickness increases, the number of percolation paths increases too sharply, leading to important conductance variations. When e reach a sufficient value, the tin dioxide structure is regular and the electrical conductivity becomes independant of the thickness.

This result can be compared with the sensitivity dependance with the thickness (figure 7). Indeed, we can see that the thinnest films (200 to 500 Å), which are supposed to be the most porous, are very sensitive to gas adsorption effects.

Conclusion

Tin dioxide films are elaborated by a chemical vapor deposition method. An accurate control of the deposition parameters (temperature, total pressure, duration), so that appropriate annealing conditions (duration, temperature), can be used to modify the structural properties of the films : grain size, thickness, stoichiometry. Important modifications of the electrical performances of tin dioxide films for gas sensing applications are observed. The main results are :

- a sharp increase of the electrical conductance under pure air G_0 with the apparition of a conduction channel inside agglomerates of grains. This corresponds to a depletion layer $L \approx 35 \text{ \AA}$
- in the 100 - 300 \AA grain size range, a predominant effect of the stoichiometry variation, leading to a decrease of G_0
- a strong influence of the film thickness, with a maximum of sensitivity for the thinner films, where tin dioxide is the most discontinuous and porous, and an increase of G_0 with e due to the increase of the number of the percolation paths up to 3000 \AA .

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